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# (54) BORON-FREE GLASS FIBERS

BORFREIE GLASFASERN

FIBRES DE VERRE SANS BORE

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- **DATABASE WPI Section Ch, Week 9534 Derwent Publications Ltd., London, GB; Class F01, AN 95-262260 XP002085808 -& RU 2 027 687 C (FOKIN A I), 27 January 1995**



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## Description

[0001] This invention relates to continuous glass fibers having glass compositions that are boron-free-i.e., essentially free of boron. The glass fibers are useful as reinforcement and textile glass fibers.

[0002] The standard glass composition for making continuous glass fiber strands is "E" glass, which dates back to the 1940's. Despite the passing of fifty years, E glass, which is generally described in U.S. Patent No. 2,334,961, still is the most common glass for making textile and reinforcement glass fibers. The key advantage of E glass is that its liquidus temperature is 200°F (111°C) below its forming temperature, the temperature at which the viscosity of the glass is customarily near 1000 poise.

[0003] E glass melts and refines at relatively low temperatures. E glass has a workable viscosity over a wide range of relatively low temperatures, a low liquidus temperature range, and a low devitrification rate. Generally, these glass compositions allow operating temperatures for producing glass fibers around 1900°F to 2400°F (1038°C to 1316°C) where the liquidus temperature is approximately 2100°F (1149°C) or lower. Industry typically maintains a fiber-forming temperature around 100°F (56°C) greater than the liquidus temperature for continuous fiber production in order to avoid devitrification in the glass delivery system and bushing.

[0004] In the mid 1970's, boron- and fluorine-containing glasses were developed which met these operating conditions. See U.S. Patent No. 4,026,715. However, boron and fluorine in glass melts are volatile components that contribute significantly to the total emissions evolved from a glass melting operation.

[0005] Glass compositions free of boron or fluorine are known, e.g., as disclosed in British Patent Specification No. 520,427. However, known boron- and fluorine-free glass compositions have posed problems.

[0006] Such textile glasses as disclosed in British Patent Specification No. 520,427 melt and form at higher temperatures requiring operating conditions which could not be practically met. Devitrification (crystallization) in the bushing or during forming often occurred. For example, British Patent Specification No. 520,247 discloses glass compositions that are substantially alkaline-free containing CaO, MgO, $Al_2O_3$, and $SiO_2$, that may be modified by the addition of $B_2O_3$, $CaF_2$, $P_2O_5$, or a small amount of an alkali such as $Na_2O$, $K_2O$, or lithia. However, only a few of these fiberize, and only the boron-containing glasses fiberize in a continuous fiber process without difficulty. Glass No. 1 on page 2 of the British reference is one of the boron-free glasses which could be fiberized in a continuous fiber process by virtue of its 100°F (56°C) difference between its liquidus and forming temperatures, but its forming temperature, at 2350°F (1288°C), is too high to be formed according to earlier known processes. The viscosity of Glass No. 2 in the British reference is 1000 poise at a temperature only 87°F (48°C) above the liquidus temperature. This probably would result in devitrification during forming in continuous glass fiber production. British Patent No. 520,247 teaches that this glass is preferably for insulating wool glasses, which can be formed with smaller differences between the liquidus and forming temperatures than can continuous fibers. Glass No. 3 is also preferably for insulating wool glasses. The liquidus temperature of Glass No. 3 of the British reference is 52°F (29°C) above the forming temperature and would crystallize in the bushing in a continuous fiber operation.

[0007] U.S. Patent No. 4,542,106 to Sproull discloses boron- and fluorine-free glass fiber compositions. In general, they contain 58 to 60 percent $SiO_2$, 11 to 13 percent $Al_2O_3$, 21 to 23 percent CaO, 2 to 4 percent MgO, and 1 to 5 percent $TiO_2$. The glass fiber compositions may also contain alkali metal oxide and trace quantities of $Fe_2O_3$. The glasses, in addition to being free of boron and fluorine and having significant $TiO_2$ present, have electrical leakage characteristics such that they can be used in lieu of standard E and "621" glasses (621 glasses are generally described in U.S. Patent No. 2,571,074). U.S. Patent No. 3,847,627 to Erickson et al. also discloses fiberizable glass compositions that are free of boron and fluorine and contain a significant amount of $TiO_2$. The Erickson et al. compositions (similar compositions are described also in British Patent Specification No. 1,391,384) consist essentially of, by weight, 54.5 to 60 percent $SiO_2$, 9 to 14.5 percent $Al_2O_3$, 17 to 24 percent CaO, 2 to 4 percent $TiO_2$, 1.5 to 4 percent MgO, and 1 to 5.5 percent of ZnO, SrO, or BaO. The use of significant amounts of titania ($TiO_2$), however, has drawbacks. For instance, a significant amount of $TiO_2$ can impart an undesirable color to the glass.

[0008] To reduce the cost of manufacturing glass fibers, and to reduce environmental pollution without increasing production costs, there is still a need in the art for improved glass compositions that are essentially free of boron and fluorine but avoid undue discoloration and still retain advantageous properties akin to E glass, and may readily be fiberized in a continuous fiber operation.

[0009] The present invention seeks to achieve economically and environmentally desirable glass fibers with advantageous properties, having low or no boron and fluorine levels and that may be fiberized without great difficulty and is based in part on the discovery that the sulfate level must be reduced in the batch in order to effectively melt and form glasses having compositions generally similar to those described in British Patent No. 520,247. The glass compositions of the present invention, however, surprisingly result in larger differences between the forming and liquidus temperatures (i.e., wider delta T values) enabling successful fiberization of a glass with exceptional properties.

[0010] The glass fibers of the invention, which are suitable for textile and reinforcement glass fibers, generally have a glass composition consisting essentially of:

| Component | Amount (weight percent) |
|---|---|
| $SiO_2$ | 59.0 to 62.0 |
| $CaO$ | 20.0 to 24.0 |
| $Al_2O_3$ | 12.0 to 15.0 |
| $MgO$ | 1.0 to 4.0 |
| $F_2$ | 0.0 to 0.5 |
| $Na_2O$ | 0.1 to 2.0 |
| $TiO_2$ | 0.0 to 0.9 |
| $Fe_2O_3$ | 0.0 to 0.5 |
| $K_2O$ | 0.0 to 2.0 |
| $SO_3$ | 0.0 to 0.5 |

**[0011]** The total of all the components, including any trace impurities, in the composition is, of course, 100 percent by weight. The glass has a viscosity of 1000 poise at temperatures ranging from 2100°F to 2500°F (1149°C to 1371°C), and the liquidus temperature of the glass is at least 100°F (55°C) below the temperature at which the fibers are formed. Despite their high-temperature operating conditions, these glasses can be fiberized without devitrification in the bushing or at forming.

**[0012]** In a preferred embodiment, the weight percent of MgO ranges from 2.0 to 3.5.

**[0013]** In another preferred embodiment, the amounts of $SiO_2$, CaO, $Al_2O_3$, MgO, and $R_2O$ ($R_2O = Na_2O + K_2O$) in these compositions are:

| Component | Weight Percent |
|---|---|
| $SiO_2$ | 59.0-61.0 |
| $CaO$ | 21.5-22.5 |
| $Al_2O_3$ | 12.7-14.0 |
| $MgO$ | 2.5-3.3 |
| $Na_2O + K_2O$ | 0.1-2.0 |
| $TiO_2$ | 0.0-0.6 |

The viscosity of these compositions are 1000 poise at temperatures ranging from 2200°F to 2400°F (1204°C to 1316°C) and the liquidus temperatures of these compositions are at least 125°F (69°C) below the temperature for a viscosity of 1000 poise.

**[0014]** More preferably, the amounts of $SiO_2$, CaO, $Al_2O_3$, MgO, and $R_2O$ are as follows:

| Component | Weight Percent |
|---|---|
| $SiO_2$ | 59.5-60.5 |
| $CaO$ | 21.7-22.3 |
| $Al_2O_3$ | 13.0-13.5 |
| $MgO$ | 2.7-3.3 |
| $Na_2O + K_2O$ | 0.5-1.0 |

**[0015]** In an especially preferred embodiment, the $TiO_2$ content is not more than 0.6 weight percent, more preferably not more than 0.04 weight percent. In an additional preferred embodiment, the $TiO_2$ content is not more than 0.6 weight percent and the $F_2$ content is essentially zero. In another preferred embodiment, the sulfate, fluorine, and titania contents are each essentially zero.

**[0016]** In an especially preferred embodiment, continuous fiber is made having approximately the following glass composition: 60.1 % $SiO_2$; 22.1 % CaO; 13.2 % $Al_2O_3$; 3.0 % MgO; 0.2 % $K_2O$; 0.2 % $Fe_2O_3$; 0.1% $F_2$; 0.5 % $TiO_2$; and 0.6 % $Na_2O$. The glass has temperature characteristics on the order of log 3 of about 2300°F (1260°C), liquidus of about 2200°F (1200°C), and delta T of about 150°F (83°C). Such a glass also has approximately the following properties: density (of fiber; according to ASTM D1505) of about 2.62 g/ml; tensile strength at 23°C (of pristine, unsized laboratory-produced single fiber; ASTM D2101) of about 3100-3800 MPa (450-550 kpsi); elastic modulus (sonic method) of about 80-81 GPa (11.6-11.7 Mpsi); elongation at breaking (of pristine, unsized laboratory-produced single fiber;

ASTM D2101) of about 4.6%; refractive index (of pristine, unsized laboratory-produced single fiber; oil immersion) of about 1.560-1.562; thermal linear expansion at 0-300°C (of bulk annealed glass; ASTM D696) of about 6.0 x$10^{-6}$/°C; softening point (ASTM C338) of about 916°C; annealing point (ASTM C336) of about 736°C; strain point (ASTM C336) of about 691°C; dielectric constant at 23°C and 1 MHz (of bulk annealed glass; ASTM D150) of about 7.0; dissipation factor at 23°C and 1 MHz (of bulk annealed glass; ASTM D150) of about 0.001; volume resistivity (of bulk annealed glass; ASTM D257; extrapolated from measurements at elevated temperatures, 120-500°C, based on log resistivity = A/temperature + B) of about 8.1*10**26; dielectric strength at 4.8 mm thickness (of bulk annealed glass; ASTM D149) of about 8 kV/mm; percentage of original tenacity after exposure to 5% NaOH at 23°C for 28 days (of pristine, unsized laboratory-produced single fiber) of about 30.

**[0017]** The glass fiber compositions of the invention are essentially free of boron. By "essentially free" we mean that the composition contains at most only a trace quantity of the specified component, e.g., from impurities in the raw materials. In a preferred embodiment, the glass fibers are also essentially fluorine-free. In another preferred embodiment, the glass fibers are also essentially titania-free.

**[0018]** In general, fibers according to the invention may be prepared as follows. The components, which may be obtained from suitable ingredients or raw materials (e.g., sand for $SiO_2$, burnt lime for CaO, dolomite for MgO) and may optionally contain trace quantities of other components, are mixed or blended in a conventional manner in the appropriate quantities to give the desired weight percentages of the final composition. The mixed batch is then melted in a furnace or melter, and the resulting molten glass is passed along a forehearth and into fiber-forming bushings located along the bottom of the forehearth. The molten glass is pulled or drawn through holes or orifices in the bottom or tip plate of the bushing to form glass fibers. The streams of molten glass flowing through the bushing orifices are attenuated to filaments by winding a strand of the filaments on a forming tube mounted on a rotatable collet of a winding machine. The fibers may be further processed in a conventional manner suitable for the intended application.

**[0019]** The temperatures of the glass at the furnace, forehearth, and bushing are selected to appropriately adjust the viscosity of the glass. The operating temperatures may be maintained using suitable means, such as control devices. Preferably, the temperature at the front end of the melter is automatically controlled to help avoid devitrification.

**[0020]** The use of sulfate in the furnace operation helps avoid seeding or bubbling problems in the glass. When producing large-scale melts, we have found it important to add carbon to the batch to control foam levels in the furnace. Preferably the sulfate-to-carbon ratio ($SO_3$/C) in the batch is from about 0.6 to about 1.7, in contrast with E glass, which typically runs best at an $SO_3$/C = 3.0 to 10.0. The sulfate-to-carbon ratio is preferably controlled in the furnace to keep the foam at a manageable level and thereby allow heat to penetrate into the glass from the gas burners. It should be understood, however, that the compositions are preferably essentially free of sulfate, since this, like carbon, is almost completely or practically entirely eliminated from the glass during melting.

**[0021]** Furthermore, the addition of a small amount of alkali helps improve the melting rate of the batch. For example, about 0.70 weight percent $Na_2O$ may be added to facilitate melting.

**[0022]** The forehearth design should be such that throughout the forehearth the glass is kept above the liquidus temperature. The forehearth should be constructed to provide for even heating of the glass to avoid cold spots causing devitrification.

**[0023]** The improved glass compositions can be readily fiberized via recent improvements in bushing technology. See U.S. Patent Nos. 5,055,119, 4,846,865 and 5,312,470. Through such improved bushing technology, the fibers may be formed at higher temperatures with smaller differences between the forming and liquidus temperatures. In general, the bushing should be structured to provide long life and resist sagging, which is dependent on the pressure of the glass on the tip plate and the temperature. For example, the bushing can be made of a stiff alloy composition, such as one containing about 22-25% rhodium and platinum. The stiffness of the tip plate may be enhanced through the use of structural or mechanical reinforcements, such as T-gussets. The bushing screen should have high corrosion resistance, which may be accomplished, e.g., by constructing the plate screen from platinum.

**[0024]** The discussion above regarding parameters and equipment is provided to illustrate a process for making the inventive glass fibers. It should be understood that the artisan may suitably modify or optimize the process parameters and equipment in light of the specific glass fibers being made and conventional design considerations.

**[0025]** The invention will now be illustrated through the following exemplary embodiments.

Example I

**[0026]** Four production samples of reinforcement glass fibers were produced with an average glass composition analyzed as consisting essentially of, by weight: 60.01 % $SiO_2$; 22.13 % CaO; 12.99 % $Al_2O_3$; 3.11 % MgO; 0.04% $F_2$; 0.63 % $Na_2O$; 0.55 % $TiO_2$; 0.25 % $Fe_2O_3$; 0.14 % $K_2O$; and 0.02% $SO_3$. On average, the forming temperature for a viscosity of 1000 poise ("log 3") was 2298°F (1259°C), the liquidus temperature was 2146°F (1174°C), and the forming-liquidus temperature difference ("delta T") was 135°F (75°C).

Example II

[0027] Using a laboratory melter, glass fibers were produced from reagents providing the following batch composition, with percentages being by weight: 60.08 % $SiO_2$; 22.07 % CaO; 13.21 % $Al_2O_3$; 3.01 % MgO; 0.16 % $K_2O$; 0.23 % $Fe_2O_3$; 0.05 % $SO_3$; 0.06% $F_2$; 0.52 % $TiO_2$; and 0.60 % $Na_2O$. The resulting glass had the following temperature properties: log 3 = 2309°F (1265°C); liquidus = 2156°F (1180°C); and delta T = 153°F (85°C).

[0028] The glass fibers were prepared as follows. Approximately 30 grams of glass cullet produced by melting reagent-grade chemicals corresponding to the above-identified composition in a platinum crucible were charged into a 1-inch (2.54-cm) diameter, resistively heated bushing. The glass was heated for an hour at a temperature of 100°C above the forming temperature. The temperature of the bushing was then reduced to the forming temperature, and fibers were produced by pulling the glass through a single orifice in the bushing onto a winder. It should be noted that although a minute quantity of sulfate (SO,) was added to help prevent seeding/bubbling problems in the glass, essentially all of the sulfate would have been driven off with the bubbles during heating of the glass batch.

Examples III-VIII

[0029] In a manner analogous to that described in Example II, glass fibers were prepared from the batch compositions (with percentages being by weight) shown in the table below.

| Example No. | III* | IV* | V* | VI* | VII | VIII |
|---|---|---|---|---|---|---|
| % $SiO_2$ | 59.45 | 61.05 | 59.05 | 59.05 | 59.45 | 59.96 |
| % CaO | 22.69 | 22.29 | 24.29 | 22.29 | 22.69 | 22.18 |
| % $Al_2O_3$ | 13.48 | 13.08 | 13.08 | 15.08 | 13.48 | 13.19 |
| % MgO | 3.23 | 2.83 | 2.83 | 2.83 | 3.23 | 3.07 |
| % $K_2O$ | 0.63 | 0.23 | 0.23 | 0.23 | 0.23 | 0.25 |
| % $Fe_2O_3$ | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 | 0.28 |
| % $SO_3$ | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| % $F_2$ | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.09 |
| % $TiO_2$ | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.37 |
| % $Na_2O$ | 0.03 | 0.03 | 0.03 | 0.03 | 0.43 | 0.55 |
| Log 3 | 2308°F (1264°C) | 2334°F (1279°C) | 2279°F (1248°C) | 2353°F (1289°C) | 2298°F (1259°C) | 2310°F (1266°C) |
| Liquidus | 2180°F (1193°C) | 2161°F (1183°C) | 2136°F (1169°C) | 2227°F (1219°C) | 2171°F (1188°C) | 2181°F (1194°C) |
| Delta T | 128°F (71°C) | 173°F (96°C) | 143°F (79°C) | 127°F (71°C) | 127°F (71°C) | 129°F (72°C) |

* Examples III-VI are Reference Examples

Example IX

[0030] Glass fibers were prepared having the following composition with essentially zero fluorine, sulfate, and titania levels: 61.00 % $SiO_2$; 22.24 % CaO; 12.00 % $Al_2O_3$; 3.25 % MgO; 0.52 % $K_2O$; 0.30 % $Fe_2O_3$; 0.00 % $SO_3$; 0.00 % $F_2$; 0.00 % $TiO_2$; and 0.69 % $Na_2O$. The glass had the following temperature characteristics: log 3 = 2304°F (1262°C); liquidus = 2203°F (1206°C); and delta T = 101°F (56°C).

[0031] As is understood in the art, the above exemplary compositions do not always total precisely 100% of the listed components due to statistical conventions (e.g., rounding and averaging). Of course, the actual amounts of all components, including any impurities, in a specific composition always total to 100%.

[0032] Furthermore, it should be understood that where small quantities of components are specified in the compositions, e.g., quantities on the order of about 0.05 weight percent or less, those components may be present in the form of trace impurities present in the raw materials, rather than intentionally added. Moreover, components may be added to the batch composition, e.g., to facilitate processing, that are later eliminated, resulting in a glass composition that is essentially free of such components. Thus, for instance, although minute quantities of components such as fluorine and sulfate have been listed in various examples, the resulting glass composition may be essentially free of such components-e.g., they may be merely trace impurities in the raw materials for the silica, calcium oxide, alumina, and magnesia components in commercial practice of the invention or they may be processing aids that are essentially

removed during manufacture.

[0033] As apparent from the above examples, glass fiber compositions or the invention have advantageous properties, such as low viscosities and wide (high) delta T values.

## Claims

1. A continuous glass fiber having a composition essentially free of boron and consisting essentially of the following components in the specified weight percentage amounts:

| | |
|---|---|
| $SiO_2$ | 59.0 to 62.0 |
| CaO | 20.0 to 24.0 |
| $Al_2O_3$ | 12.0 to 15.0 |
| MgO | 1.0 to 4.0 |
| $F_2$ | 0.0 to 0.5 |
| $Na_2O$ | 0.1 to 2.0 |
| $TiO_2$ | 0.0 to 0.9 |
| $Fe_2O_3$ | 0.0 to 0.5 |
| $K_2O$ | 0.0 to 2.0 |
| $SO_3$ | 0.0 to 0.5 |

the weight percentage of all components, including any trace impurities summing to 100 and the composition having a viscosity of 1000 poise at a forming temperature of 2100 to 2500°F (1149 to 1371°C) and a liquidus temperature at least 100°F (55°C) below the forming temperature.

2. A continuous glass fiber according to claim 1, having a MgO content of 2.0 to 3.5 weight percent.

3. A continuous glass fiber according to claim 1 or claim 2, containing the following components in the specified weight percentage amounts:

| | |
|---|---|
| $SiO_2$ | 59.0-61.0 |
| CaO | 21.5-22.5 |
| $Al_2O_3$ | 12.7-14.0 |
| MgO | 2.5-3.3 |
| $Na_2O + K_2O$ | 0.1-2.0 |
| $TiO_2$ | 0.0-0.6 |

the composition having a viscosity of 1000 poise at a forming temperature of 2200 to 2400°F (1204 to 1316°C) and a liquidus temperature at least 125°F (69°C) below the forming temperature.

4. A continuous glass fiber according to claim 3, containing the following components in the specified weight percentage amounts:

| | |
|---|---|
| $SiO_2$ | 59.5-60.5 |
| CaO | 21.7-22.3 |
| $Al_2O_3$ | 13.0-13.5 |
| MgO | 2.7-3.3 |
| $Na_2O + K_2O$ | 0.5-1.0 |

5. A continuous glass fiber according to claim 4, containing the following components in the specified weight percentage amounts:

| | |
|---|---|
| $SiO_2$ | 60.1 |
| CaO | 22.1 |

(continued)

| | |
|---|---|
| $Al_2O_3$ | 13.2 |
| MgO | 3.0 |
| $Na_2O + K_2O$ | 0.8 |

6. A continuous glass fiber according to claim 1, having a $TiO_2$ content of not more than 0.6 weight percent.

7. A continuous glass fiber according to any one of claims 1 to 6, having a $TiO_2$ content of 0.00 to 0.04 weight percent.

8. A continuous glass fiber according to any one of claims 1 to 6, having $SO_3$, $F_2$ and $TiO_2$ contents each of no more than 0.05 weight percent.

9. A continuous glass fiber according to any one of claims 1 to 8, having a $F_2$ content of 0.00 to 0.04 weight percent.

10. A continuous glass fiber according to any one of claims 1 to 9, which is essentially free of $TiO_2$.

11. A continuous glass fiber according to any one of claims 1 to 10, which is essentially free of $F_2$.

12. A continuous glass fiber according to any one of claims 1 to 11, which is essentially free of $SO_3$.

13. A continuous glass fiber according to any one of claims 1 to 12, having a liquidus temperature at least 150°F (83°C) below the forming temperature.

14. A continuous glass fiber according to claim 5, containing the following components in the specified weight percentage amounts:

| | |
|---|---|
| $K_2O$ | 0.2 |
| $Na_2O$ | 0.6 |
| $Fe_2O_3$ | 0.2 |
| $SO_3 + F_2$ | 0.1 |
| $TiO_2$ | 0.5 |

the composition having a forming temperature of 2300 to 2400°F (1204 to 1316°C) and a liquidus temperature at least 150°F (83°C) below the forming temperature.

**Patentansprüche**

1. Endlosglasfaser mit einer im wesentlichen borfreien Zusammensetzung, die im wesentlichen die folgenden Bestandteile in den angegebenen Gewichtsprozentmengen enthält:

| | |
|---|---|
| $SiO_2$ | 59,0 bis 62,0 |
| CaO | 20,0 bis 24,0 |
| $Al_2O_3$ | 12,0 bis 15,0 |
| MgO | 1,0 bis 4,0 |
| $F_2$ | 0,0 bis 0,5 |
| $Na_2O$ | 0,1 bis 2,0 |
| $TiO_2$ | 0,0 bis 0,9 |
| $Fe_2O_3$ | 0,0 bis 0,5 |
| $K_2O$ | 0,0 bis 2,0 |
| $SO_3$ | 0,0 bis 0,5 |

wobei die Gewichtsprozente aller Bestandteile einschließlich Spuren von Verunreinigungen sich zu 100 addieren und die Zusammensetzung eine Viskosität von 1000 Poise bei einer Formgebungstemperatur von 2100 bis 2500°F

(1149 bis 1371°C) und eine Liquidustemperatur von zumindest 100°F (55°C) unterhalb der Verformungstemperatur besitzt.

2. Endlosglasfaser nach Anspruch 1 mit einem MgO-Gehalt von 2,0 bis 3,5 Gewichtsprozent.

3. Endlosglasfaser nach Anspruch 1 oder 2, die die folgenden Bestandteile in den angegebenen Gewichtsprozentmengen enthält:

| | |
|---|---|
| $SiO_2$ | 59,0 bis 61,0 |
| CaO | 21,5 bis 22,5 |
| $Al_2O_3$ | 12,7 bis 14,0 |
| MgO | 2,5 bis 3,3 |
| $Na_2O + K_2O$ | 0,1 bis 2,0 |
| $TiO_2$ | 0,0 bis 0,6 |

wobei die Zusammensetzung eine Viskosität von 1000 Poise bei einer Verformungstemperatur von 2200 bis 2400°F (1204 bis 1316°C) und eine Liquidustemperatur von zumindest 125°F (69°C) unterhalb der Verformungstemperatur besitzt.

4. Endlosglasfaser nach Anspruch 3 mit den folgenden Bestandteilen in den angegebenen Gewichtsprozentmengen:

| | |
|---|---|
| $SiO_2$ | 59,5 bis 60,5 |
| CaO | 21,7 bis 22,3 |
| $Al_2O_3$ | 13,0 bis 13,5 |
| MgO | 2,7 bis 3,3 |
| $Na_2O + K_2O$ | 0,5 bis 1,0 |

5. Endlosglasfaser nach Anspruch 4 mit den folgenden Bestandteilen in den angegebenen Gewichtsprozentmengen:

| | |
|---|---|
| $SiO_2$ | 60,1 |
| CaO | 22,1 |
| $Al_2O_3$ | 13,2 |
| MgO | 3,0 |
| $Na_2O + K_2O$ | 0,8 |

6. Endlosglasfaser nach Anspruch 1 mit einem $TiO_2$-Gehalt von höchstens 0,6 Gewichtsprozent.

7. Endlosglasfaser nach einem der Ansprüche 1 bis 6 mit einem $TiO_2$-Gehalt von 0,00 bis 0,04 Gewichtsprozent.

8. Endlosglasfaser nach einem der Ansprüche 1 bis 6 mit $SO_3$-, $F_2$- und $TiO_2$-Gehalten von jeweils höchstens 0,05 Gewichtsprozent.

9. Endlosglasfaser nach einem der Ansprüche 1 bis 8 mit einem $F_2$-Gehalt von 0,00 bis 0,04 Gewichtsprozent.

10. Endlosglasfaser nach einem der Ansprüche 1 bis 9, die im wesentlichen frei von $TiO_2$ ist.

11. Endlosglasfaser nach einem der Ansprüche 1 bis 10, die im wesentlichen frei von $F_2$ ist.

12. Endlosglasfaser nach einem der Ansprüche 1 bis 11, die im wesentlichen frei von $SO_3$ ist.

13. Endlosglasfaser nach einem der Ansprüche 1 bis 12 mit einer Liquidustemperatur von mindestens 150°F (83°C) unterhalb der Verformungstemperatur.

14. Endlosglasfaser nach Anspruch 5 mit den folgenden Bestandteilen in den angegebenen Gewichtsprozentmengen:

| | |
|---|---|
| $K_2O$ | 0,2 |
| $Na_2O$ | 0,6 |
| $Fe_2O_3$ | 0,2 |
| $SO_3 + F_2$ | 0,1 |
| $TiO_2$ | 0,5 |

wobei die Zusammensetzung eine Verformungstemperatur von 2300 bis 2400°F (1204 bis 1316°C) und eine Liquidustemperatur von mindestens 150°F (83°C) unterhalb der Verformungstemperatur besitzt.

**Revendications**

1. Fibre de verre continue ayant une composition sensiblement exempte de bore et constituée essentiellement des composants suivants, dans les quantités en pourcentages en poids spécifiées :

| | |
|---|---|
| $SiO_2$ | 59,0 à 62,0 |
| CaO | 20,0 à 24,0 |
| $Al_2O_3$ | 12,0 à 15,0 |
| MgO | 1,0 à 4,0 |
| $F_2$ | 0,0 à 0,5 |
| $Na_2O$ | 0,1 à 2,0 |
| $TiO_2$ | 0,0 à 0,9 |
| $Fe_2O_3$ | 0,0 à 0,5 |
| $K_2O$ | 0,0 à 2,0 |
| $SO_3$ | 0,0 à 0,5 |

les pourcentages en poids de tous les composants, y compris les impuretés à l'état de traces, s'élevant à 100 et la composition ayant une viscosité de 1000 poises à une température de mise en forme de 1149 à 1371°C (2100 à 2500°F), et une température de liquidus au moins 55°C (100°F) au-dessous de la température de mise en forme.

2. Fibre de verre continue selon la revendication 1, ayant une teneur en MgO de 2,0 à 3,5 % en poids.

3. Fibre de verre continue selon la revendication 1 ou la revendication 2, contenant les composants suivants, dans les quantités en pourcentages en poids spécifiées :

| | |
|---|---|
| $SiO_2$ | 59,0 à 61,0 |
| CaO | 21,5 à 22,5 |
| $Al_2O_3$ | 12,7 à 14,0 |
| MgO | 2,5 à 3,3 |
| $Na_2O + K_2O$ | 0,1 à 2,0 |
| $TiO_2$ | 0,0 à 0,6 |

la composition ayant une viscosité de 1000 poises à une température de mise en forme de 1204 à 1316°C (2200 à 2400°F), et une température de liquidus au moins 69°C (125°F) au-dessous de la température de mise en forme.

4. Fibre de verre continue selon la revendication 3, contenant les composants suivants, dans les quantités en pourcentages en poids spécifiées :

| | |
|---|---|
| $SiO_2$ | 59,5 à 60,5 |
| CaO | 21,7 à 22,3 |
| $Al_2O_3$ | 13,0 à 13,5 |
| MgO | 2,7 à 3,3 |
| $Na_2O + K_2O$ | 0,5 à 1,0 |

**5.** Fibre de verre continue selon la revendication 4, contenant les composants suivants, dans les quantités en pourcentages en poids spécifiées :

| | |
|---|---|
| $SiO_2$ | 60,1 |
| CaO | 22,1 |
| $Al_2O_3$ | 13,2 |
| MgO | 3,0 |
| $Na_2O + K_2O$ | 0,8 |

**6.** Fibre de verre continue selon la revendication 1, ayant une teneur en $TiO_2$ qui n'est pas supérieure à 0,6 % en poids.

**7.** Fibre de verre continue selon l'une quelconque des revendications 1 à 6, ayant une teneur en $TiO_2$ de 0,00 à 0,04 % en poids.

**8.** Fibre de verre continue selon l'une quelconque des revendications 1 à 6, ayant des teneurs en $SO_3$, $F_2$ et $TiO_2$ qui ne sont pas supérieures, chacune, à 0,05 % en poids.

**9.** Fibre de verre continue selon l'une quelconque des revendications 1 à 8, ayant une teneur en $F_2$ de 0,00 à 0,04 % en poids.

**10.** Fibre de verre continue selon l'une quelconque des revendications 1 à 9, qui est sensiblement exempte de $TiO_2$.

**11.** Fibre de verre continue selon l'une quelconque des revendications 1 à 10, qui est sensiblement exempte de $F_2$.

**12.** Fibre de verre continue selon l'une quelconque des revendications 1 à 11, qui est sensiblement exempte de $SO_3$.

**13.** Fibre de verre continue selon l'une quelconque des revendications 1 à 12, ayant une température de liquidus au moins 83°C (150°F) au-dessous de la température de mise en forme.

**14.** Fibre de verre continue selon la revendication 5, contenant les composants suivants dans les quantités en pourcentages en poids spécifiées :

| | |
|---|---|
| $K_2O$ | 0,2 |
| $Na_2O$ | 0,6 |
| $Fe_2O_3$ | 0,2 |
| $SO_3 + F_2$ | 0,1 |
| $TiO_2$ | 0,5 |

la composition ayant une température de mise en forme de 1204 à 1316°C (2300 à 2400°F) et une température de liquidus au moins 83°C (150°F) au-dessous de la température de mise en forme.